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Errata to Figures 9 and 10

On figure 9 on the curves reading from top to bottom, the temperatures should be 5[illegible]°, 473°, 373°, and 293° respectively.

On figure 10, curve A is at the top and curve C is at the bottom.

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THE INTERMOLECULAR POTENTIALS OF HELIUM AND HYDROGEN*
(and force constants for some non polar molecules)

by

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I. Introduction

Recently, the transport property collision integrals and the second virial coefficients have been evaluated[1][2] for gases whose molecules obey an "Exp-Six" intermolecular potential

$$\varphi(r) = \frac{\epsilon}{1-6/\alpha}\left[\frac{6}{\alpha}\, e^{\alpha(1-r/r_m)} - \left(\frac{r_m}{r}\right)^6\right], \tag{1}$$

where $\varphi(r)$ is the potential energy of two molecules at a separation distance r, ϵ is the depth of the potential energy minimum, r_m is the position of the minimum, and α is a parameter which is a measure of the steepness of the repulsion energy. The form of this potential has some theoretical justification in that the inverse sixth power term represents the leading term in the expression for the attractive London dispersion potential, and the

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(1) E. A. Mason, J. Chem. Phys. 22, 000 (1954).

(2) W. E. Rice and J. O. Hirschfelder, J. Chem. Phys. 22, 000 (1954).

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exponential term is indicated by quantum-mechanical calculations of the repulsive potential between molecules. The representation of the total intermolecular potential by Eq. (1) is, however, probably to be considered semi-empirical at best. The parameters ϵ, r_m, and α may be determined for a particular gas by comparison of the experimentally observed transport properties and second virial coefficients with the theoretical tabulations given in references (1) and (2). The best previous potential for which similar theoretical calculations have been performed is of the Lennard-Jones (12-6) form

$$\varphi(r) = \epsilon\left[\left(\frac{r_m}{r}\right)^{12} - 2\left(\frac{r_m}{r}\right)^{6}\right] , \tag{2}$$

where $\varphi(r)$, ϵ, and r_m are as defined in connection with Eq. (1). This potential has had some success in correlating transport properties and compressibilities of simple gases, but has not been completely satisfactory for a number of gases. Two particular cases are helium and hydrogen, in which it appears that the intermolecular repulsion is actually "softer" than indicated by an inverse twelfth power. In the present paper we report the analysis of the available experimental data on these two gases to determine the appropriate values of the parameters of Eq. (1), and a discussion of the ability of this potential form to correlate the properties of these gases.

A table of potential energy constants for other simple non polar molecules is given in the appendix.

II. Determination of Potential Parameters.

Several different methods are available for the determination of the potential parameters from experimental results on compressibilities[(3)-(6)] and transport properties[(6)-(9)]. The method we have used is an adaptation of the Keesom and Lennard-Jones procedure[(3)] for the second virial coefficient, and is simple, accurate, and permits the simultaneous fit of several different gas properties with relatively little calculation. We have applied this method to experimental second virial coefficient and viscosity data to evaluate the potential parameters for helium and hydrogen. Data are also available on the other transport properties of thermal conductivity, self-diffusion, and thermal

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(3) W. H. Keesom, Leiden Comm. Suppl. No. 25 (1912); J. E. Lennard-Jones, Proc. Roy. Soc. (Lond.) A106, 463 (1924).

(4) R. A. Buckingham, Proc. Roy. Soc. (Lond.) A168, 264 (1938).

(5) W. H. Stockmayer and J. A. Beattie, J. Chem. Phys. 10, 476 (1942).

(6) Hirschfelder, Curtiss, Bird, and Spotz, The Molecular Theory of Gases and Liquids. (John Wiley and Sons, New York, 1954), Chapters 3 and 8.

(7) H. R. Hasse and W. R. Cook, Phil. Mag. 3, 978 (1927); Proc. Roy. Soc. (Lond.) A125, 196 (1929).

(8) E. Whalley and W. G. Schneider, J. Chem. Phys. 20, 657 (1952).

(9) Amdun, Ross, and Mason, J. Chem. Phys. 20, 1620 (1952).

diffusion, but these data are usually rather scanty and of poor accuracy compared with those on viscosity, and we have not used them directly in assigning potential parameters. However, they serve as a check on the parameters determined from the second virial coefficient and viscosity.

The method used is as follows:

The second virial coefficient $B(T)$ of a pure gas is given by

$$B(T) = b_m B^*(\alpha, T^*) \quad , \tag{3}$$

with
$$b_m = (2\pi\, No/3)\, r_m^3 \quad , \tag{4}$$

and
$$T^* = kT/\epsilon \quad , \tag{5}$$

where No is the Avogadro number, k is the Boltzmann constant, T is the absolute temperature, and α, r_m, and ϵ are the parameters given in Eq. (1). The quantity $B^*(\alpha, T^*)$ is tabulated in reference (2) as a function of T^* for several values of α. Taking logarithms of Eqs. (3) and (5), we obtain

$$\log B(T) = \log B^*(\alpha, T^*) + \log b_m \quad , \tag{6}$$

$$\log T = \log T^* + \log(\epsilon/k). \tag{7}$$

A plot of the tabulated quantities $\log B^*(\alpha, T^*)$ vs. $\log T^*$ yields a family of curves, one for each value of α. From Eqs. (6) and (7) it is seen that a plot of the experimental quantities $\log B(T)$ vs. $\log T$ should be superposable by parallel translation of axes on one of the theoretical curves, and that $\log b_m$ is directly determined by the amount of translation parallel

to the B-axis, and $\log(\epsilon/k)$ by the amount of translation parallel to the T-axis. The parameter r_m is then found from Eq. (4), and the third parameter α has of course already been determined by the decision to superpose the experimental plot on a particular one of the family of theoretical curves.

An analogous procedure may be used to determine α, r_m, and ϵ from experimental viscosity measurements. In practical units, the viscosity η of a pure gas is given by

$$10^7\eta = \frac{266.93\,(MT)^{\frac{1}{2}}}{r_m^2}\;\frac{f_\eta^{(3)}(\alpha, T^*)}{\Omega^{(2,2)*}(\alpha, T^*)} ; \tag{8}$$

where η is the viscosity in grams-cm^{-1}-sec^{-1}, M is the molecular weight, r_m is in angstroms, and $f_\eta^{(3)}(\alpha, T^*)$ and $\Omega^{(2,2)*}(\alpha, T^*)$ are dimensionless functions which may be obtained from the tabulations in reference (2). Taking logarithms of Eqs. (8) and (5), we obtain

$$\log \frac{10^7\eta}{(MT)^{\frac{1}{2}}} = \log \frac{f_\eta^{(3)}}{\Omega^{(2,2)*}} + \log(266.93) - 2\log r_m , \tag{9}$$

$$\log T = \log T^* + \log(\epsilon/k).$$

as with the second virial coefficient, a plot of the theoretical quantities $\log\left[f_\eta^{(3)}/\Omega^{(2,2)*}\right]$ vs. $\log T^*$ yields a family of curves, over one of which may be superposed by parallel translation of axes the plot of the experimental quantities $\log\left[10^7\eta/(MT)^{\frac{1}{2}}\right]$ vs. $\log T$. The amount of

translation along the η-axis determines log r_m, the amount of translation along the T-axis determines log (ϵ/k), and the decision to superpose on a particular theoretical curve determines α.

The above procedures were carried out for helium and hydrogen. Most of the experimental viscosity values were determined relative to the viscosity of air, and it was necessary to reduce them to a common basis. For this purpose the viscosity of air was taken as η = 1833.0 x 10^{-7} gm $-cm^{-1}-sec^{-1}$ at 23°C, following Johnston and McCloskey[10] None of the necessary corrections were as large as one percent. It should be pointed out that neither the viscosity data nor the second virial coefficient data alone are sufficient to determine three potential parameters uniquely for either helium or hydrogen, but that both properties must be considered together. For example, the parameter α may be assigned uniquely on the basis of the viscosity results, but a number of different pairs of values of the parameters ϵ and r_m would serve equally well to fit the experimental points. On the other hand, the second virial coefficients have not been measured accurately over a sufficiently wide temperature range to enable a unique assignment of the parameter α to be made.

The determination of the potential parameters for helium and hydrogen is complicated by the fact that these gases exhibit large quantum deviations. Even at room temperature the quantum correction to the second virial coefficient of hydrogen amounts to several percent. Kirkwood[11] and Uhlenbeck and

(10) H. L. Johnston and K. E. McCloskey, J. Phys. Chem. 44, 1038 (1940).

(11) J. G. Kirkwood, Phys. Rev. 44, 31 (1933).

Beth[12] have shown that for the second virial coefficient the quantum deviations may be expressed as an infinite series in powers of h^2, where h is Planck's constant. For the exp-six potential, the expression for the second virial coefficient including quantum corrections may be written as

$$B(T) = B_{cl}(T) + h^2 B_I(T) + h^4 B_{II}(T) + ---,$$
$$= b_o \left[B^*(\alpha, T^*) + (\Lambda^2/T^*) B_I^*(\alpha, T^*) + (\Lambda^2/T^*)^2 B_{II}^*(\alpha, T^*) + --- \right], \tag{10}$$

where $B(T)$, b_o, $B^*(\alpha, T^*)$, and T^* are as defined in connection with Eqs. (3)-(5), Λ is the dimensionless group $h/\left[r_m(m\epsilon)^{\frac{1}{2}} \right]$, where m is the mass of one molecule, and $B_I^*(\alpha, T^*)$ and $B_{II}^*(\alpha, T^*)$ are integrals involving the intermolecular potential, $\varphi(r)$. The convergence of this series is poor except when (Λ^2/T^*) is small and hence it cannot be used at low temperatures for helium and hydrogen. The integrals B_I^* and B_{II}^* have not been evaluated for the exp-six potential, but B_I^* has been calculated for the Buckingham-Corner potential[13]. This potential differs from Eq. (1) only for $r < r_m$, in which region the inverse sixth power term is multiplied by an exponential term to prevent $\varphi(r)$ from becoming negative for very small values of r. Thus, in the region of the minimum, the exp-six and the Buckingham-Corner potentials are nearly identical, and since this portion of

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(12) G. E. Uhlenbeck and E. Beth, Physica 3, 729 (1936).

(13) R. A. Buckingham and J. Corner, Proc. Roy. Soc. (Lond) A189, 118 (1947).

the potential contributes most strongly to $B(T)$ at temperatures low enough for quantum deviations to be appreciable, it seems reasonable to use the tables of Buckingham and Corner to determine the first quantum correction, $b_o(\Lambda^2/T^*)B_1^*$, for the exp-six potential. The first quantum correction is tabulated in reference (13) as the function $F_1(\alpha, x)$, given as

$$F_1(\alpha, x) = (2\pi/3)\, B_I^*(\alpha, T^*), \tag{11}$$

where $x = 1/T^*$.

Inclusion of the quantum correction necessitates a small change in the curve-fitting procedure outlined above for determining the potential parameters ϵ, r_m, and α from experimental values of $B(T)$. The quantity Λ is first assumed to be zero, and the method of translation of axes applied to obtain a first approximation to ϵ, r_m, and α. From these values a first approximation to Λ is calculated, which is substituted into Eqs. (10) and (11), and the entire procedure repeated to obtain second approximations to ϵ, r_m, and α. A new value of Λ is then calculated, and the procedure repeated until Λ no longer varies. It turns out that the first quantum corrections for helium and hydrogen calculated in this way are very nearly equal to those calculated for these gases by de Boer and Michels[14] according to the Lennard-Jones (12-6) potential given in Eq. (2). It therefore seems reasonable to make the assumption that the second quantum corrections, $b_o(\Lambda^2/T^*)^2 B_2^*$, are

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(14) J. de Boer and A. Michels, Physica 5, 945 (1938).

also nearly equal for the two potentials, and to take the small values of the second quantum corrections from the tabulations of de Boer and Michels. The lack of exact values for the second quantum correction limits the usable temperature region to values above 60°K for helium and above 120°K for hydrogen.

The quantum deviations for the transport properties may also be expressed as a power series in h^2, as shown by de Boer and Bird[15][16]. In this case, unfortunately, very few numerical calculations have been made, so the best we can do at present is to obtain a rough estimate of the temperature range for which quantum deviations from the transport properties are negligible. The reduced collision integral for viscosity, $\Omega^{(2,2)*}(\alpha, T^*)$, which is given in Eq. (8), may be modified to include quantum effects as follows:

$$\Omega^{(2,2)*}(\alpha, T^*) = \Omega_{cl}^{(2,2)*}(\alpha, T^*) + (\Lambda^2/T^*)\Omega_{I}^{(2,2)*}(\alpha, T^*) + \cdots , \tag{12}$$

where $\Omega_{cl}^{(2,2)*}$ is the classical contribution to the total reduced collision integral, tabulated in reference (1). Λ and T^* are as previously defined, and $\Omega_{I}^{(2,2)*}$ is a very complicated integral involving the intermolecular potential. The only potential for which $\Omega_{I}^{(2,2)*}$ has been evaluated[16] is

$$\varphi(r) = \epsilon \left(\frac{r_m}{r}\right)^{12} , \tag{13}$$

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(15) J. de Boer and R. B. Bird, Phys. Rev. 83, 1259 (1951).

(16) Reference (6), Chapter 10.

which is the form assumed by the Lennard-Jones (12-6) potential of Eq. (2) when there is no intermolecular attraction. Since in helium and hydrogen the intermolecular attraction is small, it seems reasonable to use Eq. (13) to obtain a rough estimate of the quantum corrections, using the values of ϵ and r_m for the Lennard-Jones (12-6) potential found by de Boer and Michels[14] from analysis of second virial coefficients. In this way it is found that the quantum deviations of the viscosity, thermal conductivity, and self-diffusion are less than about 0.6 percent for temperatures above 200°K and 250°K for helium and hydrogen, respectively.

The values of the potential parameters of the exp-six potential and the quantum-mechanical parameter Λ for helium and hydrogen found by the above procedure are given in Table I. Also included are the values of these quantities for the Lennard-Jones (12-6) potential as found by de Boer and Michels[14] and revised by Lunbeck[17]. These Lennard-Jones parameters have been shown to give reasonable agreement with experiment on helium for very low temperature second virial coefficients[18], viscosities, and thermal conductivities[19], and for higher temperature viscosities and thermal conductivities[20], as well as reasonable agreement on hydrogen for very low

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(17) R. J. Lunbeck, Dissertation Amsterdam (1951), has revised the the parameters found by de Boer and Michels to take account of more recent values of the fundamental constants k, No, and h. See reference (6) for a compilation of these revised parameters.

(18) J. de Boer and A. Michels, Physica 6, 409 (1939).

(19) J. de Boer, Physica 10, 348 (1943).

(20) J. de Boer and J. van Kranendonk, Physica 14, 442 (1948).

temperature second virial coefficients and viscosities[21], and higher temperature viscosities[20]. Thus, these Lennard-Jones parameters are probably the best available for helium and hydrogen.

Table 1

Potential parameters for the exp-six and Lennard-Jones (12-6) potentials for helium and hydrogen, and the quantum-mechanical parameter $\Lambda \cdot h/[r_m(m\epsilon)^{\frac{1}{2}}]$.

	Helium		Hydrogen	
	Exp-Six	L.-J. (12-6)	Exp-Six	L.-J. (12-6)
α	12.4	-	14.0	-
r_m, Å	3.135	2.869	3.337	3.287
ϵ/k, °K	9.16	10.22	37.3	37.0
Λ	2.305	2.385	1.512	1.541

III. Comparison with Experiment

A check on the validity of using the parameters determined for the exp-six potential to calculate the first quantum correction for the second virial coefficient from the tables for the Buckingham-Corner potential may be obtained from a consideration of hydrogen and deuterium. Since the intermolecular

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(21) R. Miyako, Proc. Phys. - Math Soc. (Japan) 24, 852 (1942).

potential for hydrogen is the same as that for deuterium[14],[22],[23], the virial coefficients of hydrogen and deuterium differ only because of quantum effects, and we, therefore, obtain from Eq. (10) the relation

$$B(H_2) - B(D_2) = (b_0/T^*)[\Lambda^2(H_2) - \Lambda^2(D_2)] B_I^*(\alpha, T^*) + \ldots, \qquad (13)$$

where $B(H_2)$ and $B(D_2)$ are the second virial coefficients, and $\Lambda(H_2)$ and $\Lambda(D_2)$ are the quantum mechanical parameters for hydrogen and deuterium. In Figure 1 we plot the values of $[B(H_2) - B(D_2)]$ as a function of temperature as found from the compressibility measurements of Michels and Goudeket[24], along with the theoretical curve obtained from Buckingham and Corner's tables by using the exp-six potential parameters in Table I. The agreement between theory and experiment provides some justification for our procedure. It is true that the theoretical curve was obtained under the assumption that hydrogen and deuterium could be considered as spherical molecules, but de Boer[25] has shown that the values of $[B(H_2) - B(D_2)]$ calculated in this way do not differ significantly from the values obtained when hydrogen and deuterium are treated as non-spherical diatomic molecules.

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(22) A. B. van Cleave and O. Maass, Am. J. Res. B13, 384 (1935).

(23) H. W. Woolley, R. B. Scott, and F. G. Brickwedde, J. Res. Nat. Bur. Stds. 41, 379 (1948) have summarized most of the evidence for this conclusion.

(24) A. Michels and M. Goudeket, Physica 8, 347, 353 (1941). We have used the second virial coefficients obtained by fitting the experimental PV values between 9 and 32 atm. with a quadratic series in the density.

(25) J. de Boer, Physica 10, 357 (1943).

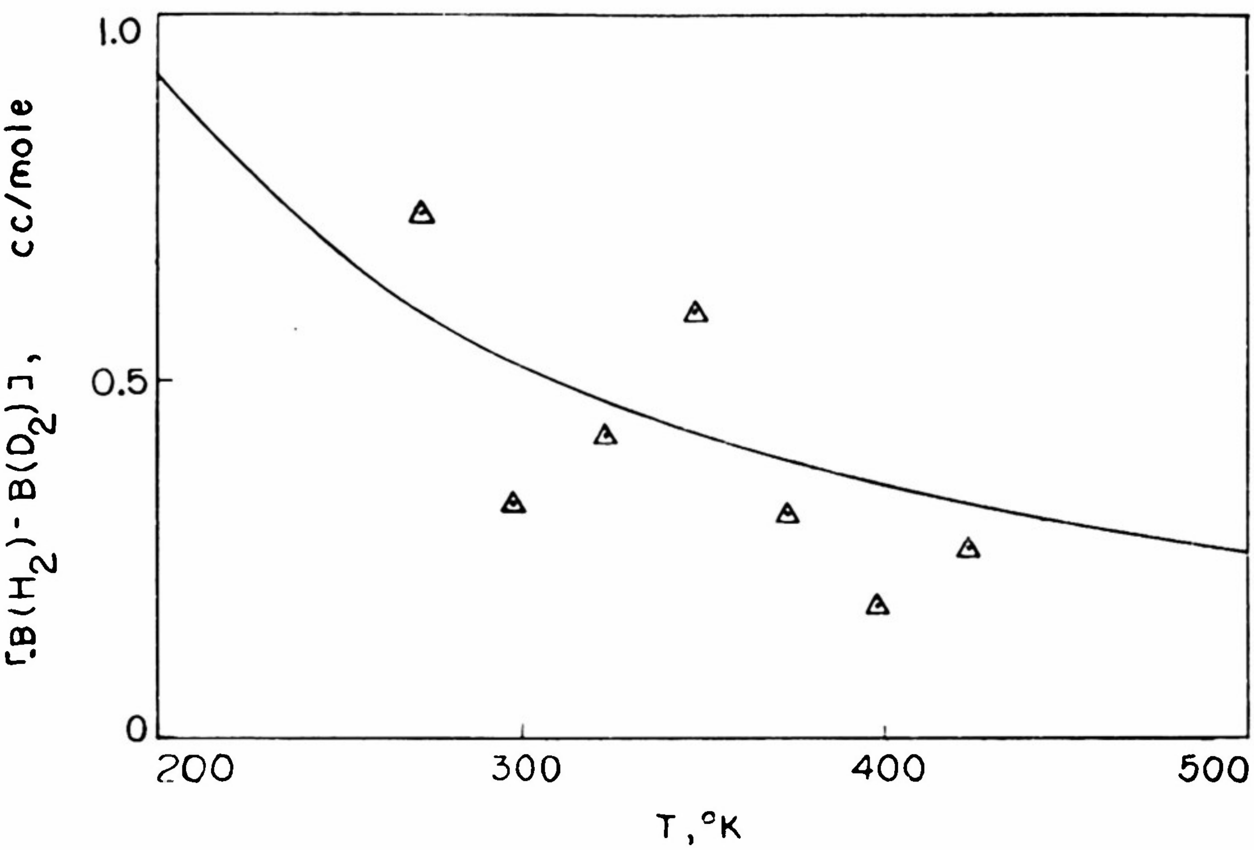

Fig. 1. Comparison of experimental and theoretical values of the quantum correction to the second virial coefficient of hydrogen. The experimental points are from the data of Michels and Goudeket[24]; the calculated curve is from the tables of Buckingham and Corner[13] using the parameters of Table I.

A. Helium

To illustrate the suitability of the exp-six form for describing the intermolecular potential of helium, we have used the potential parameters listed in Table I to calculate a number of properties of gaseous helium for comparison with experimental results. Second virial coefficients of helium have been measured from 65.2° to 1473.2°K. Figure 2 shows a comparison of calculated and experimental[26] values; also shown in the figure is the theoretical curve for the Lennard-Jones (12-6) potential of Table I. Below 273.2°K the experimental values are in poor agreement and the exp-six and Lennard-Jones (12-6) potentials do about equally well in fitting the data, but at high temperatures the exp-six gives a definitely superior fit; helium atoms are clearly "softer" than indicated by the (12-6) potential. The agreement between experimental values and those calculated from the exp-six potential is shown in more detail in Table II for temperatures above 273.2°K. The maximum deviation is 0.34 cc/mole, and the average absolute deviation is 0.18 cc/mole. This is satisfactory agreement since experimental second virial coefficients are seldom more accurate than this[24][27].

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(26) J. D. A. Boks and H. K. Onnes, Leiden Comm. 170a (1924); L. Holborn and J. Otto, Z. Physik 10, 367 (1922); 23,77 (1924); 33, 1 (1925); 38, 359 (1926); G. P. Nijhoff and W. H. Keesom, Leiden Comm. 188b (1927); Nijhoff, Keesom, and Illin, ibid. 188c (1927); Gibby, Tanner, and Masson, Proc. Roy. Soc. (London) A122, 283 (1929); A. Michels and H. Wouters, Physica 8, 923 (1941); W. G. Schneider and J. A. H. Duffie, J. Chem. Phys. 17, 751 (1949); J. L. Yntema and W. G. Schneider, ibid 18, 641 (1950). The results of Gibby, Tanner, and Masson are not shown in Figure 1 because they are essentially duplicated by those of Michels and Wouters.

(27) Hirschfelder, McClure, and Weeks, J. Chem. Phys. 10, 201 (1942).

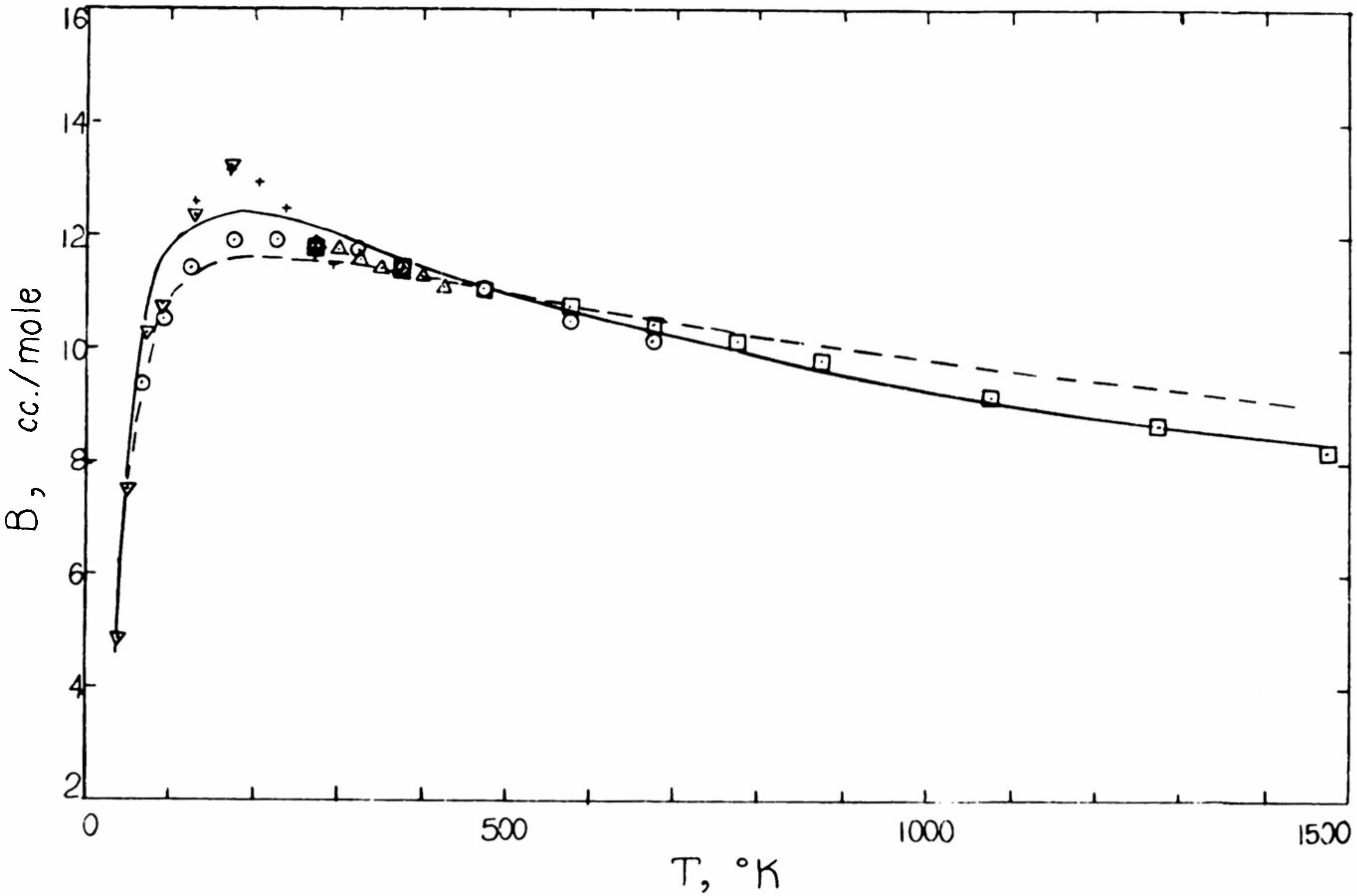

Fig. 2. Comparison of observed and calculated values of the second virial coefficient of helium. Solid line: exp-six potential; broken line: Lennard-Jones (12-6) potential. Observed values: + Boks and Onnes; ▽ Nijhoff, Keesom, and Iliin; ⊙ Holborn and Otto; ▲ Michels and Wouters; ⊡ Schneider, Duffie, and Yntema.

Table II

Comparison of observed second virial coefficients of helium with those calculated for the exp-six potential.

T, °K	B(T), cc/mole		
	Calc.	Obs.	Deviation, cc/mole
273.2	12.11	11.86[a]	-0.25
		11.87[b]	-0.24
		11.77[c]	-0.34
298.2	11.99	11.74[b]	-0.25
323.2	11.86	11.74[a]	-0.12
		11.58[b]	-0.28
348.2	11.73	11.43[b]	-0.30
373.2	11.60	11.39[a]	-0.21
		11.35[b]	-0.25
		11.42[c]	-0.18
398.2	11.48	11.24[b]	-0.24
423.2	11.36	11.07[b]	-0.29
473.2	11.12	11.07[a]	-0.05
		11.08[c]	-0.04
573.2	10.71	10.50[a]	-0.21
		10.76[c]	+0.05
673.2	10.33	10.14[a]	-0.19
		10.45[c]	+0.12
773.2	9.99	10.14[c]	+0.15
873.2	9.68	9.82[c]	+0.14
		9.80[d]	+0.12
1073.2	9.11	9.17[d]	+0.06
1273.2	8.69	8.66[d]	-0.03
1473.2	8.33	8.19[d]	-0.24

a. L. Holborn and J. Otto, Z. Physik 10, 367 (1922); 23, 77 (1924); 33, 1 (1925); 38, 359 (1926).

b. A. Michels and H. Wouters, Physica 8, 923 (1941).

c. W. G. Schneider and J. A. H. Duffie, J. Chem. Phys. 17, 751 (1949).

d. J. L. Yntema and W. G. Schneider, ibid 18, 641 (1950).

Figure 3 shows a similar comparison of calculated and experimental[28] viscosities for helium. Only the data of Trautz and Binkele, Trautz and Zink, Trautz and Heberling, Trautz and Husseini, Wobser and Müller, and Johnston and Grilly are shown; values obtained by other workers are in satisfactory agreement with these. The agreement is excellent at higher temperatures; the deviations below about 200°K are presumably due to quantum effects. Calculations for the Lennard-Jones (12-6) are also shown in the figure; here again it is seen that the inverse twelfth power repulsion is too steep for helium. Table III gives a more detailed comparison between calculated and experimental values for temperatures above 200°K; in all cases the agreement is within the consistency of the experimental data.

If the exp-six potential is to be considered satisfactory, it should be able to predict other properties than second virial coefficients and viscosities. For helium, experimental results suitable for comparison with theoretical calculations are available for the properties of thermal conductivity and thermal diffusion. The thermal conductivity of a monatomic gas may be written as

$$\lambda = \frac{5}{2}\eta \frac{C_v}{M} \frac{f_\lambda^{(3)}}{f_\eta^{(3)}} , \tag{14}$$

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(28) Y. Ishida, Phys. Rev. 21, 550 (1923); M. N. States, Phys. Rev. 21, 662 (1923); A. G. Nasini and C. Rossi, Gazz. Chim. Ital. 58, 433, 898 (1928); M. Trautz and H. E. Binkele, Ann. Physik 5, 561 (1930); M. Trautz and R. Zink, ibid 7, 427 (1930); M. Trautz and R. Heberling, ibid 20, 118 (1934); M. Trautz and I. Husseini, ibid 20, 121 (1934); M. Trautz and H. Zimmerman, ibid 22, 189 (1935); A. van Itterbeek and W. H. Keesom, Physica 5, 257 (1938); A. van Itterbeek and O. van Paemel, Physica 7, 265 (1940); R. Wobser and F. Müller, Kolloid-Beihefte 52, 165 (1941); H. L. Johnston and E. R. Grilly, J. Phys. Chem. 46, 948 (1942); van Itterbeek, van Paemel, and van Lierde, Physica 13, 88 (1947).

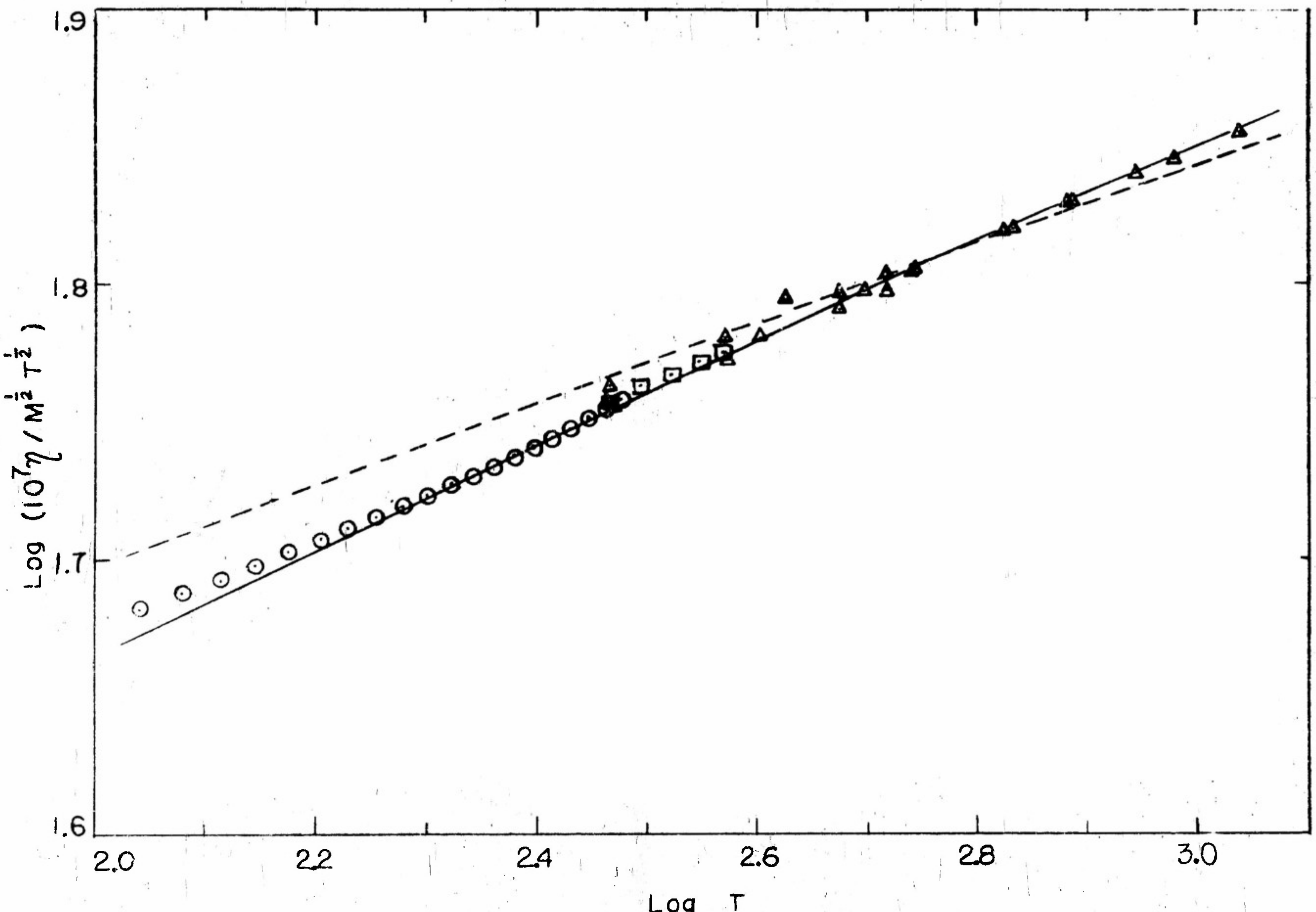

Fig. 3. Comparison of observed and calculated values of the viscosity of helium. Solid line: exp-six potential; broken line: Lennard-Jones (12-6) potential. Observed values: △ Trautz, et al; ⊡ Wobser and Mueller; ⊙ Johnston and Grilly.

Table III

Comparison of observed viscosities of helium with those calculated for the exp-six potential.

T, °K	$10^7\eta$, $gm\text{-}cm^{-1}\text{-}sec^{-1}$		
	Calc.	Obs.	% Dev.
200	1491	1496[f]	+0.34
210	1542	1546[f]	+0.26
220	1593	1594[f]	+0.06
230	1644	1644[f]	0
240	1692	1692[f]	0
250	1740	1740[f]	0
260	1789	1788[f]	+0.05
270	1837	1838[f]	+0.05
280	1884	1888[f]	+0.21
290	1929	1937[f]	+0.41
291.8	1937	1956[b]	+0.98
293	1943	1951[c]	+0.41
		1953[d]	+0.51
293.2	1944	1984[a]	+2.06
		1960[e]	+0.82
294.6	1950	1960[b]	+0.51
300	1975	1987[f]	+0.61
313.2	2034	2051[e]	+0.84
333.2	2123	2139[e]	+0.75
353.2	2211	2225[e]	+0.63
371.2	2288	2300[e]	+0.52
373	2295	2297[d]	+0.09
373.2	2296	2320[a]	+1.57
400	2409	2416[c]	+0.29
423.2	2504	2565[a]	+2.44
473	2702	2687[d]	-0.56
473.2	2703	2729[a]	+0.96
500	2805	2806[c]	+0.04
523	2893	2871[d]	-0.76
523.2	2894	2918[a]	+0.83
550	2997	2992[c]	-0.17
554	3012	3013[b]	+0.03
555	3015	3007[b]	-0.26

Table III (continued)

T, °K	$10^7 \eta$, gm-cm^{-1}-sec^{-1}		
	Calc.	Obs.	% Dev.
665	3408	3405[b]	-0.09
680	3460	3453[b]	-0.20
759	3728	3724[b]	-0.11
767	3754	3748[b]	-0.16
879	4115	4107[b]	-0.19
881	4121	4113[b]	-0.19
949	4334	4324[b]	0.23
955	4353	4338[b]	-0.34
1088	4753	4726[b]	-0.57
1090	4760	4736[b]	-0.50

a. M. Trautz and H. E. Binkele Ann. Physik <u>5</u>, 561 (1930).

b. M. Trautz and R. Zink, <u>ibid</u> <u>7</u>, 427 (1930).

c. M. Trautz and R. Heberling, <u>ibid</u> <u>20</u>, 118 (1934).

d. M. Trautz and I. Husseini, <u>ibid</u> <u>20</u>, 121 (1934).

e. R. Wobser and F. Müller, Kolloid-Beihefte <u>52</u>, 165 (1941).

f. H. L. Johnston and E. R. Grilly, J. Phys. Chem. <u>46</u>, 948 (1942).

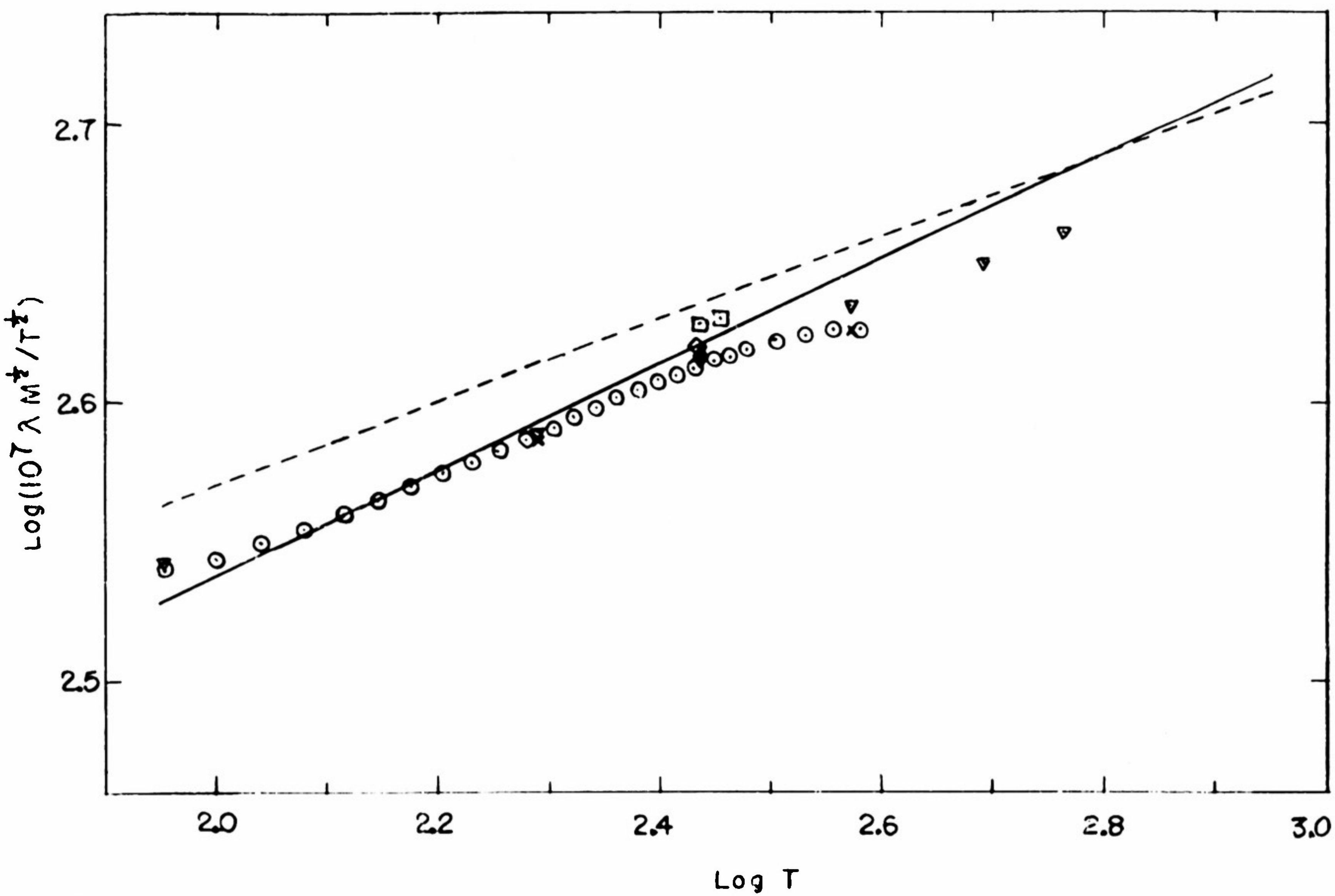

Fig. 4. Comparison of observed and calculated values of the thermal conductivity of helium. Solid line: exp-six potential; broken line: Lennard-Jones (12-6) potential. Observed values: × Eucken; ◇ Weber; □ Dickins; △ Kannuluik and Martin; ⊙ Johnston and Grilly; ▽ Kannuluik and Carman.

where λ is the thermal conductivity, η is the viscosity as given by Eq. (8), C_v is the molar heat capacity of the gas, M is the molecular weight, and $f_\lambda^{(3)}$ and $f_\eta^{(3)}$ are functions tabulated in reference (1). The ratio $(f_\lambda^{(3)}/f_\eta^{(3)})$ is very close to unity. Figure 4 shows a comparison between experimental[29] thermal conductivities and those calculated from Eq. (14) for the exp-six and Lennard-Jones (12-6) potentials. The exp-six potential given somewhat better results, but the agreement between theory and experiment is certainly not outstanding, the discrepancies being usually larger than the estimated experimental error. However, it should be pointed out that the discrepancies are not the fault of the potential, but rather of the basic theory itself, since measured values of λ, η, and C_v are not consistent with Eq. (14) for any reasonable values of the f's. This disagreement between experiment and the fundamental theory, if real and not due to unexpectedly large experimental errors, is certainly surprising.

A property which is quite sensitive to the intermolecular potential is the thermal diffusion factor. Different theoretical expressions are available for this quantity, depending on the approximation procedures used. According

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(29) A. Eucken, Physik. Z. 12, 1101 (1911); 14, 324 (1913); S. Weber, Ann. Physik 54, 437 (1917); B. G. Dickins, Proc. Roy. Soc. (London) A143, 517 (1934); W. G. Kannuluik and L. H. Martin, Proc. Roy. Soc. (London) A144, 496 (1934); H. L. Johnston and E. R. Grilly, J. Chem. Phys. 14, 233 (1946); W. G. Kannuluik and E. H. Carman, Proc. Phys. Soc. (London) B65, 701 (1952).

to the procedure of Chapman and Cowling[30], the m th approximation to the thermal diffusion factor of a binary gas mixture, $[\alpha_T]_m$, is given by the expression

$$[\alpha_T]_m = \frac{5}{2} \frac{x_1\left(\frac{M_1+M_2}{2M_1}\right)^{\frac{1}{2}} \mathscr{A}_{01}^{(m)} + x_2\left(\frac{M_1+M_2}{2M_2}\right)^{\frac{1}{2}} \mathscr{A}_{0-1}^{(m)}}{x_1 x_2 \mathscr{A}_{00}^{(m)}}, \tag{15}$$

where x_1 and x_2 are the mole fractions of gas 1 and gas 2 of the binary mixture, and M_1 and M_2 are the molecular weights. The three terms of the form $\mathscr{A}_{ij}^{(m)}$ are minors of a (2m + 1)-order determinant $\mathscr{A}^{(m)}$. The general element of $\mathscr{A}^{(m)}$ is a_{ij}, where i and j range from -m to m, and is a complicated function of the composition of the mixture, the molecular weights of the component gases, and the intermolecular forces. The minor $\mathscr{A}_{ij}^{(m)}$ is obtained from $\mathscr{A}^{(m)}$ by deleting the row and column containing a_{ij}. Expressions for the a_{ij} for m = 2 are given in reference (1), as well as tables for evaluating the a_{ij} for the special case of the exp-six potential. For m = 1, Eq. (15) may be written in the handier form,

$$[\alpha_T]_1 = (6C^* - 5) \frac{x_1 S_1 - x_2 S_2}{x_1^2 Q_1 + x_2^2 Q_2 + x_1 x_2 Q_{12}}, \tag{16}$$

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(30) S. Chapman and T. G. Cowling, The Mathematical Theory of Non-Uniform Gases (Cambridge University Press, Teddington, England, second edition, 1952), page 149.

where

$$S_1 = \frac{M_1}{M_2}\left(\frac{2M_2}{M_1+M_2}\right)^{\frac{1}{2}}\left[\frac{\Omega_{11}^{(2,2)*}}{\Omega_{12}^{(1,1)*}}\right]\left[\frac{(r_m)_{11}}{(r_m)_{12}}\right]^2 - \frac{4M_1M_2}{(M_1+M_2)^2}A^* - \frac{15M_2(M_2-M_1)}{(M_1+M_2)^2},$$

$$Q_1 = \frac{2}{M_2(M_1+M_2)}\left(\frac{2M_2}{M_1+M_2}\right)^{\frac{1}{2}}\left[\frac{\Omega_{11}^{(2,2)*}}{\Omega_{12}^{(1,1)*}}\right]\left[\frac{(r_m)_{11}}{(r_m)_{12}}\right]^2\left[3M_2^2+\left(\frac{5}{2}-\frac{6}{5}B^*\right)M_1^2 + \frac{8}{5}M_1M_2A^*\right]$$

$$Q_{12} = \frac{15(M_1-M_2)^2}{(M_1+M_2)^2}\left(\frac{5}{2}-\frac{6}{5}B^*\right) + \frac{4M_1M_2}{(M_1+M_2)^2}\left(11-\frac{12}{5}B^*\right)A^*$$
$$+\left(\frac{8}{5}\right)\frac{M_1+M_2}{(M_1M_2)^{\frac{1}{2}}}\left[\frac{\Omega_{11}^{(2,2)*}}{\Omega_{12}^{(1,1)*}}\right]\left[\frac{\Omega_{22}^{(2,2)*}}{\Omega_{12}^{(1,1)*}}\right]\left[\frac{(r_m)_{11}(r_m)_{22}}{(r_m)_{12}^2}\right]^2,$$

and A^*, B^*, C^*, and the $\Omega^{(\ell,n)*}$ are functions tabulated in reference (1). The subscripts refer to the molecular species, and the relations for S_2 and Q_2 are obtained from those for S_1 and Q_1 by an interchange of subscripts. The subscripts on the $\Omega^{(\ell,n)*}$ and the r_m refer to the three different molecular interactions which must be considered in a binary gas mixture, two involving like molecules (1, 1) and (2, 2), and the third involving unlike molecules (1, 2). For isotopes, the distinction does not arise, since intermolecular forces are presumably the same between different isotopic species.

Kihara[31] observed that the elements a_{ij} are small unless $i = j$, and performed an expansion of Eq. (15) in powers of the a_{ij}, keeping no terms of order higher than a_{ij}^2 $(i \neq j)$. In this way he arrived at an expression for the first approximation to α_T of the same form as Eq. (16), but with the following expressions for the Q's:

$$Q_1 = \frac{2}{M_2(M_1+M_2)}\left(\frac{2M_2}{M_1+M_2}\right)^{\frac{1}{2}}\left[\frac{\Omega_{11}^{(2,2)*}}{\Omega_{12}^{(1,1)*}}\right]\left[\frac{(r_m)_{11}}{(r_m)_{12}}\right]^2\left[M_1^2+3M_2^2+\frac{8}{5}M_1M_2A^*\right];$$

$$Q_{12} = \frac{15(M_1-M_2)^2}{(M_1+M_2)^2}+\frac{32M_1M_2}{(M_1+M_2)^2}A^*+\left(\frac{8}{5}\right)\frac{M_1+M_2}{(M_1M_2)^{\frac{1}{2}}}\left[\frac{\Omega_{11}^{(2,2)*}}{\Omega_{12}^{(1,1)*}}\right]\left[\frac{\Omega_{22}^{(2,2)*}}{\Omega_{12}^{(1,1)*}}\right]\left[\frac{(r_m)_{11}(r_m)_{22}}{(r_m)_{12}^2}\right]^2. \tag{17}$$

The relation for Q_2 is obtained from that for Q_1 by an interchange of subscripts.

Three expressions are thus available for the thermal diffusion factor: the first and second approximations of Chapman and Cowling, hereafter denoted respectively as $[cc]_1$ and $[cc]_2$, and the first approximation of Kihara, hereafter denoted as $[K]_1$. For helium, the thermal diffusion factor has been determined by McInteer, Aldrich and Nier[32] by measuring the thermal separation of a He^3-He^4 mixture between 273° and 613°K. Over this temperature range, they found a mean value of the thermal diffusion factor, $\bar{\alpha}_T = 0.059 \pm 0.005$, the He^3 being present in only a trace concentration.

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(31) T. Kihara, Imperfect Gases (originally published in Japanese (Asakusa Bookstore, Tokyo (1949)) and translated into English by the U. S. Office of Air Research, Wright-Patterson Air Force Base).

(32) McInteer, Aldrich, and Nier, Phys. Rev 72, 510 (1947).

According to Brown[33], this should be equal to the actual value of α_T at a mean temperature $\bar{T}$, given by

$$\bar{T} = \frac{T T'}{T' - T} \ln \frac{T'}{T}, \tag{18}$$

where T and T' are respectively the low and high temperatures involved in the thermal separation. Taking $\bar{T} = 398^\circ K$, the values calculated from the three theoretical formulas from the exp-six parameters of Table I are as follows: $[cc]_1 = 0.0532$, $[cc]_2 = 0.0599$, $[K]_1 = 0.0594$. The agreement is excellent except for $[cc]_1$, which is a little low. The value of $[K]_1$ is better than $[cc]_1$, a feature which has previously been noted for the special case of thermal diffusion in a binary mixture of heavy isotopes[1].

B. Hydrogen

The parameters of Table I have been used to calculate a number of properties of gaseous hydrogen for comparison with experimental results. Experimental values of the second virial coefficient which lie in the temperature range where comparisons are possible have been measured from 123.2° to $473.2^\circ K$. Figure 5 is a plot of experimental[34] and calculated values for both

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(33) H. Brown, Phys. Rev. 58, 661 (1940).

(34) L. Holborn and J. Otto, Ann. Physik 63, 674 (1920); Z. Physik 23, 77 (1924); 33, 1 (1925); 38, 359 (1926); G. P. Nijhoff and W. H. Keesom, Leiden Comm. 188d (1927); Gibby, Tanner, and Masson, Proc. Roy. Soc. (Lond.) A122, 283 (1929); A. Michels and M. Goudeket, reference (24).

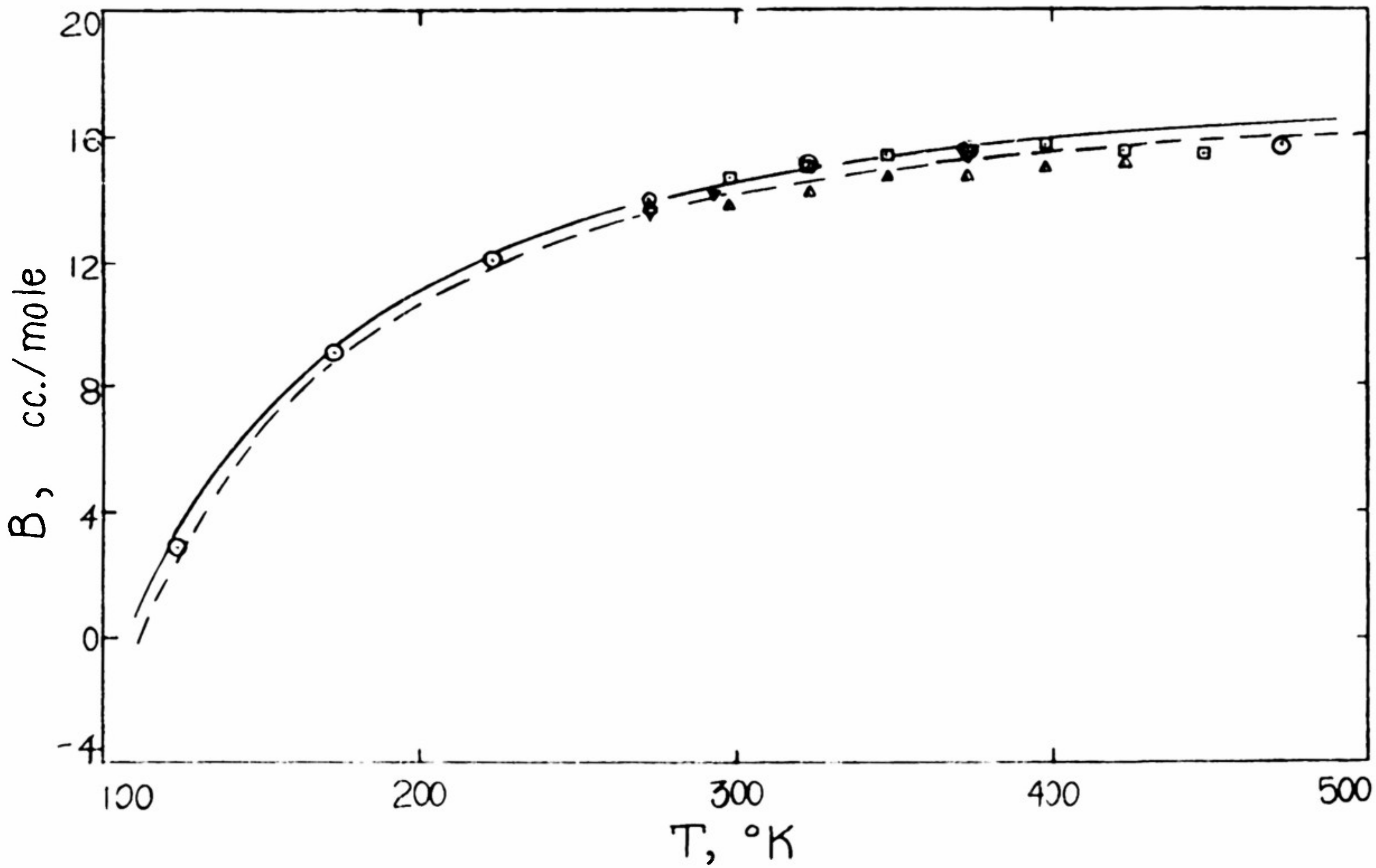

Fig. 5. Comparison of observed and calculated values of the second virial coefficient of hydrogen. Solid line: exp-six potential; broken line: Lennard-Jones (12-6) potential. Observed values: ⊙ Holborn and Otto; ▼ Nijhoff and Keesom; ⊡ Gibby, Tanner, and Masson; △ Michels and Goudeket.

the exp-six and Lennard-Jones (12-6) potential; the agreement is seen to be satisfactory for both potentials. Unlike helium, the data does not extend to high enough temperatures to show the "softness" of the repulsion energy. A more detailed comparison is given in Table IV; the maximum deviation is 0.97 cc/mole, and the average absolute deviation is 0.40 cc/mole. Thus, the agreement between theory and experiment is about as good as the agreement among different observers.

Figure 6 shows a similar comparison of experimental[35] viscosities and those calculated for the exp-six and Lennard-Jones (12-6) potential. Only a sampling of the available data is plotted; other values are in satisfactory agreement. Here we can see that hydrogen is "softer" than an inverse twelfth power repulsion, although the discrepancy is not as marked as in the

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(35) Y. Ishida, Phys. Rev. 21, 550 (1923); P. Günther, Z. Physik, Chem. 110, 626 (1924); M. Trautz and P. B. Baumann, Ann. Physik 2, 733 (1929); M. Trautz and F. W. Stauf ibid 2, 737 (1929); M. Trautz and K. F. Kipphan, ibid 2, 743 (1929); M. Trautz and W. Ludewigs, ibid 3, 409 (1929); M. Trautz and H. E. Binkele, ibid 5, 561 (1930); M. Trautz and A. Melster, ibid 7, 409 (1930); M. Trautz and R. Zink, ibid 7, 427 (1930); M. Trautz and F. Kurz, ibid 9, 981 (1931); M. Trautz and K. G. Sorg, ibid 10, 81 (1931); M. Trautz and R. Heberling, ibid 10, 155 (1931); B. P. Sutherland and O. Maass, Am. J. Res. 6, 428 (1932); M. Trautz and R. Heberling, Ann. Physik 20, 118 (1934); M. Trautz and I. Husseini, ibid 20 121 (1934); M. Trautz and H. Zimmerman, ibid 22, 189 (1935); A. van Itterbeek and A. Claes, Nature 142, 793 (1938); Physica 5, 938 (1938); A. van Itterbeek and O. van Paemel, Physica 7, 265 (1940); H. L. Johnston and K. E. McCloskey, J. Phys. Chem. 44, 1038 (1940); R. Wobser and F. Müller, Kolloid-Beihefte 52, 165 (1941); van Itterbeek, van Paemel, and van Lierde, Physica 13, 88 (1947); de Troyer, van Itterbeek, and Rietveld, ibid 17, 938 (1951); J. W. Buddenberg and C. R. Wilke, J. Phys. Coll. Chem. 55, 1491 (1951).

Table IV

Comparison of observed second virial coefficients of hydrogen with those calculated for the exp-six potential.

T, °K	B(T), cc/mole		
	Calc.	Obs.	Deviation, cc/mole
123.2	3.34	2.95[a]	-0.39
173.2	9.27	9.15[a]	-0.12
223.2	12.24	12.10[a]	-0.14
273.2	13.93	14.00[a]	+0.07
		13.58[b]	-0.35
		13.71[d]	-0.22
293.2	14.41	14.16[b]	-0.25
298.2	14.51	14.71[c]	+0.20
		13.81[d]	-0.70
323.2	14.97	15.17[a]	+0.19
		15.04[c]	+0.07
		14.21[d]	-0.76
348.2	15.34	15.37[c]	+0.03
		14.76[d]	-0.58
373.2	15.63	15.58[a]	-0.04
		15.39[b]	-0.24
		14.72[d]	-0.91
373.5	15.64	15.54[c]	-0.10
398.2	15.88	14.94[d]	-0.94
398.4	15.88	15.74[c]	-0.14
423.2	16.07	15.10[d]	-0.97
423.3	16.07	15.51[c]	-0.56
448.2	16.24	15.39[c]	-0.85
473.2	16.38	15.71[a]	-0.67

a. L. Holborn and J. Otto, Ann. Physik 63, 674 (1920), Z. Physik 23, 77 (1924); 33, 1 (1925); 38, 359 (1926).

b. G. P. Nijhoff and W. H. Keesom, Leiden Comm. 188d (1927).

c. Gibby, Tanner, and Masson, Proc. Roy. Soc. (London) A122, 283 (1929).

d. A. Michels and M. Goudeket, Physica 8, 347 (1941).

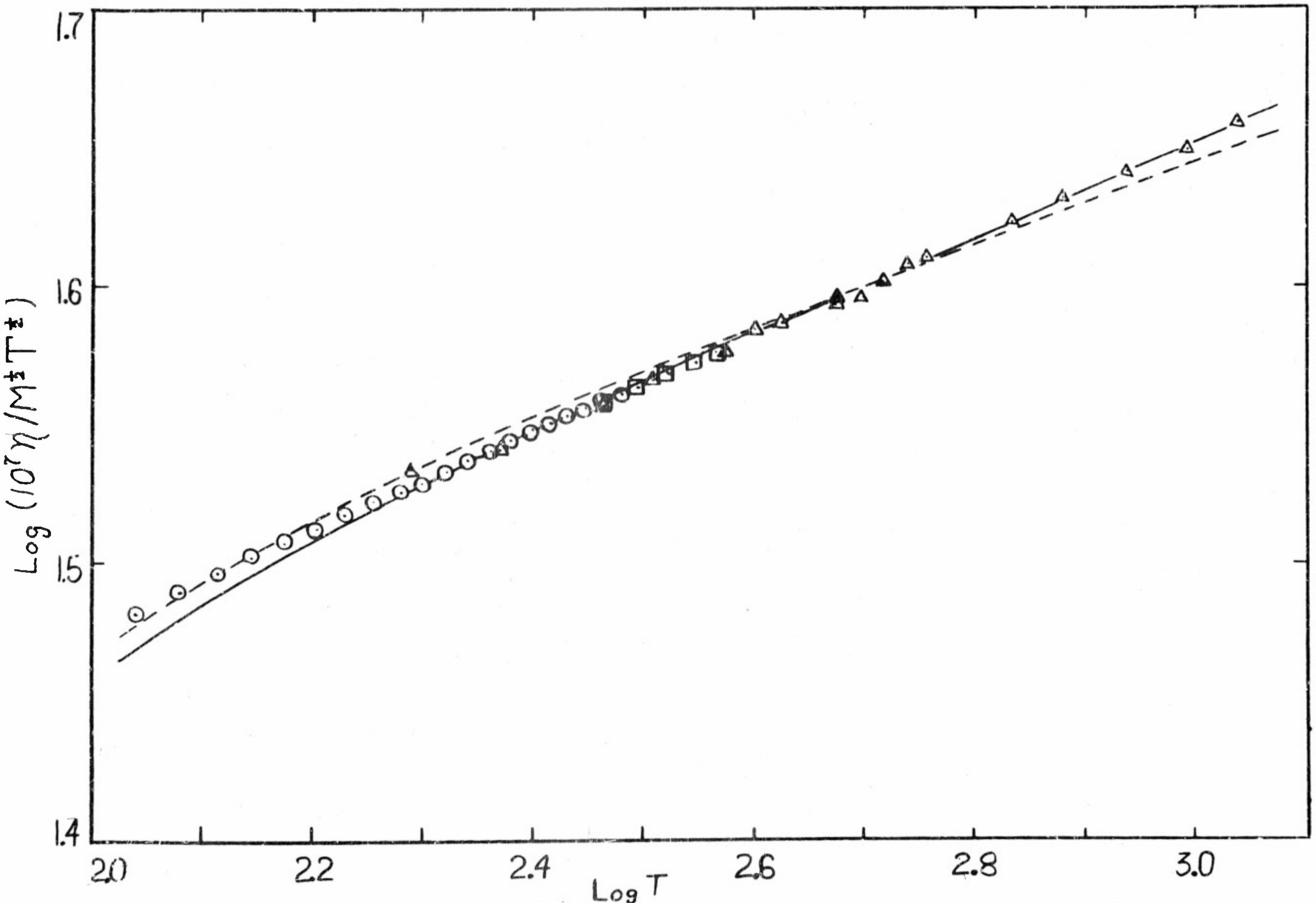

Fig. 6. Comparison of observed and calculated values of the viscosity of hydrogen. Solid line: exp-six potential; broken line: Lennard-Jones (12-6) potential. Observed values: △ Trautz, et al; ⊡ Wobser and Mueller; ⊙ Johnston and McCloskey.

case of helium. The deviations at temperatures below about 200°K are presumably due to quantum effects. Table V gives a more detailed comparison between theory and the experimental values shown in Figure 6 for temperatures above 200°K; the agreement is within the consistency of the experimental data.

Other properties of gaseous hydrogen which have been measured include thermal conductivity, self-diffusion, and thermal diffusion. Since a hydrogen molecule can transport energy in its internal degrees of freedom, the calculation of the thermal conductivity is quite uncertain, and we have not attempted to make any comparison between theory and experiment for this property.

The coefficient of self-diffusion of a gas may be written

$$D_{11} = \frac{2.6280 \times 10^{-3}\, T^{3/2}}{p M^{1/2} r_m^2} \; \frac{f_D^{(3)}(\alpha, T^*)}{\Omega^{(1,1)*}(\alpha, T^*)}, \tag{19}$$

where D_{11} is the self-diffusion coefficient in cm^2/sec, p is the pressure in atmospheres, $f_D^{(3)}(\alpha, T^*)$ and $\Omega^{(1,1)*}(\alpha, T^*)$ are dimensionless functions which may be obtained from the tabulations in reference (2), and the other quantities are as previously defined. The self-diffusion coefficient for hydrogen has been measured by following the diffusion of orthohydrogen and parahydrogen[36], and of deuterium and hydrogen[37][38]. Table VI compares the measured

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(36) P. Harteck and H. W. Schmidt, Z. Physik. Chem. B21, 447 (1933).

(37) Heath, Ibbs, and Wild, Proc. Roy. Soc. (London) A178, 380 (1941).

(38) L. Waldmann, Naturwiss 32, 223 (1944); Z. Naturforsch. 1, 59 (1946).

Table V

Comparison of observed viscosities of hydrogen with those calculated for the exp-six potential.

T, °K	$10^7 \eta$, gm-cm^{-1}-sec^{-1}		
	Calc.	Obs.	% Dev.
200	680	681[f]	+0.15
210	704	704[f]	0.00
220	727	727[f]	0.00
230	749	749[f]	0.00
235.2	761	758[a]	-0.39
240	771	771[f]	0.00
250	793	792[f]	-0.13
260	815	814[f]	-0.12
270	836	835[f]	-0.12
280	857	856[f]	-0.12
289.9	877	872[c]	-0.57
290	878	876[f]	-0.23
292.2	882	878[a]	-0.45
293	884	879[d]	-0.57
	884	880[e]	-0.45
293.2	884	879[b]	-0.57
	884	881[g]	-0.34
300	898	896[f]	-0.22
313.2	924	922[g]	-0.22
323.2	944	942[b]	-0.21
333.2	964	960[g]	-0.41
353.2	1002	999[g]	-0.30
371.2	1036	1031[g]	-0.48
373	1039	1036[e]	-0.29
373.2	1040	1035[a]	-0.48
	1040	1034[b]	-0.58
400	1090	1092[d]	+0.18
423.2	1132	1131[b]	-0.09
473	1219	1221[c]	+0.16
	1219	1216[e]	-0.25
473.2	1219	1218[a]	-0.08
	1219	1217[b]	-0.16

Table V (continued)

T, °K	$10^7 \eta$, gm-cm^{-1}-sec^{-1}		
	Calc.	Obs.	% Dev.
500	1265	1255[d]	-0.79
523	1303	1303[e]	0.00
523.2	1303	1304[a]	+0.08
	1303	1303[b]	0.00
550	1348	1352[d]	+0.30
572	1384	1388[c]	+0.30
685	1561	1562[c]	+0.06
763	1678	1680[c]	+0.12
874	1839	1838[c]	-0.05
986	1994	1992[c]	-0.10
1098	2143	2148[c]	+0.23

a. M. Trautz and P. B. Baumann. Ann. Physik 2, 733 (1929).

b. M. Trautz and H. E. Binkele, ibid 5, 561 (1930).

c. M. Trautz and R. Zink, ibid 7 427 (1930).

d. M. Trautz and R. Heberling, ibid 20, 118 (1934).

e. M. Trautz and I. Husseini, ibid 20, 121 (1934).

f. H. L. Johnston and K. E. McCloskey, J. Phys. Chem. 44, 1038 (1940).

g. R. Wobser and F. Müller, Kolloid-Beihefte 52, 165 (1941).

Table VI

Comparison of observed values of the self-diffusion coefficient of hydrogen with those calculated for the exp-six potential.

T °K	D_{11}(1 atm.), cm^2/sec.		
	Calc.	Obs.	% Dev.
85	0.162	0.169 ± 0.008[a]	+4.3
273	1.257	1.26 ± 0.04 [a]	0.0
288.2	1.379	1.43[b]	+3.6
293	1.418	1.442 ± 0.0026[a]	+1.7
293.2	1.420	1.40[c]	-1.4

a. P. Harteck and H. W. Schmidt, Z. Physik.Chem. B21, 447 (1933). These values have been recalculated to avoid an uncertain extrapolation over a temperature range performed in the original article.

b. Heath, Ibbs, and Wild, Proc. Roy. Soc. (London) A178, 380 (1941).

c. L. Woldmann, Naturwiss. 32, 223 (1944); Z. Naturforsch. 1, 59 (1946).

values with those calculated for the exp-six potential. All values refer to a pressure of 1 atmosphere. The values for the system D_2-H_2 have been corrected to refer to an ideal system in which all molecules have the same mass as normal hydrogen by multiplying by the square root of the ratio of the reduced mass of the experimental system to that of the ideal system. The correction factor is equal to 1.155 in the present case. The values are also shown in Figure 7, together with the theoretical values for the exp-six and Lennard-Jones (12-6) potentials. Within the experimental error both potentials are satisfactory.

The thermal diffusion factor, α_T, has been measured a number of times for the system D_2-H_2. The best data appear to be those of Heath, Ibbs and Wild[37], who measured thermal separations between 288° and 373°K. The same method has also been used by Grew[39] Murphey[40], and de Troyer, van Itterbeek, and Rietveld[41]. The value of α_T has also been determined from the diffusion thermo-effect by Waldmann[38]. Within the scatter of the experimental values, which is large, the various workers are in agreement with Heath, Ibbs, and Wild. The results of the latter are compared

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(39) K. E. Grew, Proc. Roy. Soc. (London) A178, 390 (1941).

(40) B. F. Murphey, Phys. Rev. 72, 834 (1947).

(41) de Troyer, van Itterbeek, and Rietveld, Physica 17, 938 (1951).

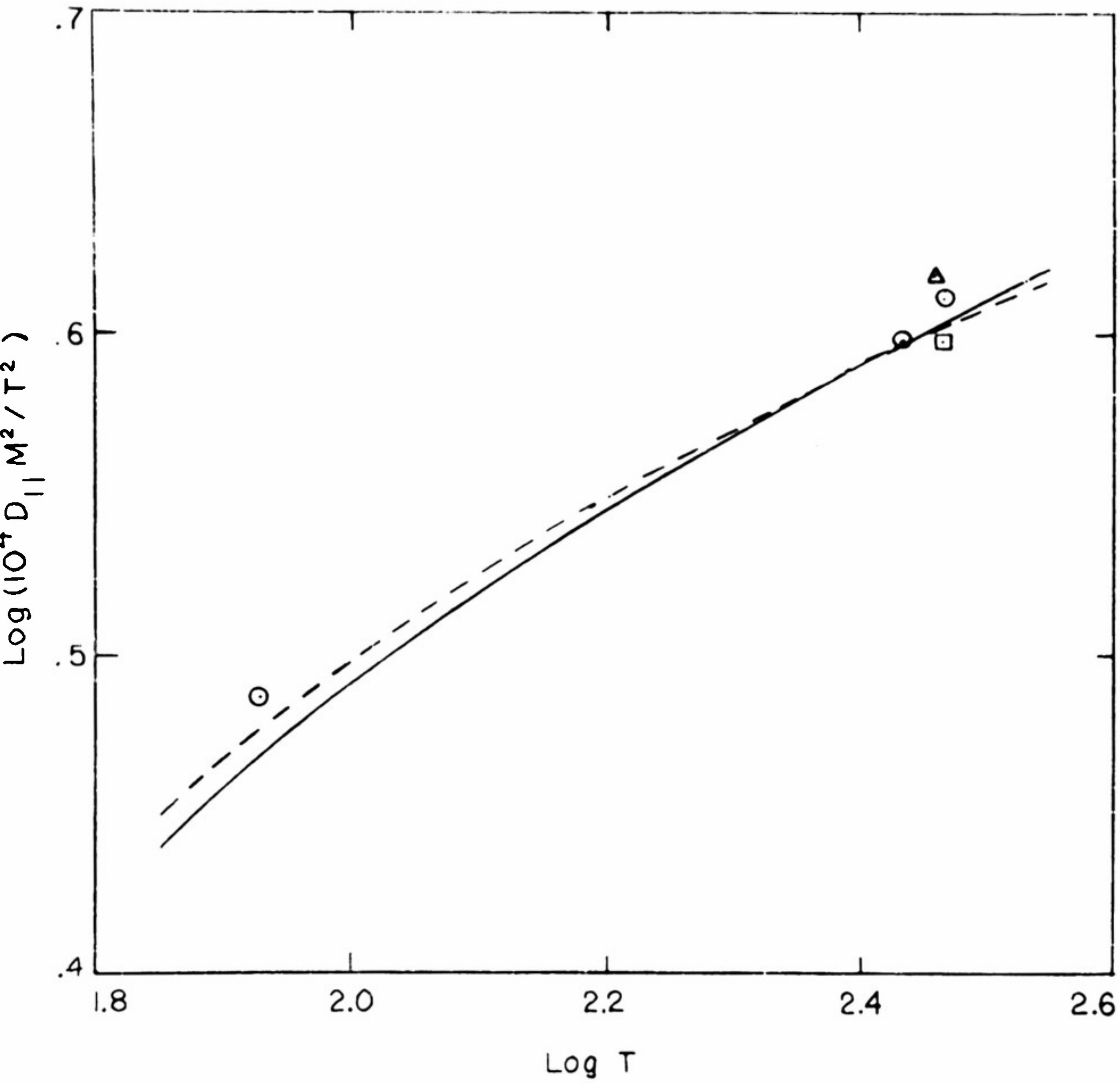

Fig. 7. Comparison of observed and calculated values of the self-diffusion coefficient of hydrogen. Solid line: exp-six potential; broken line: Lennard Jones (12-6) potential. Observed values: ○ Harteck and Schmidt, △ Heath, Ibbs, and Wild, ⊡ Waldmann.

with the theoretical calculations in Table VII where T has been taken as 327°K, according to Eq. (18). Three theoretical expressions are available, as discussed in connection with the thermal diffusion of helium. The values in Table VII are plotted in Figure 8, in which the trend of α_T with composition is more easily seen. The agreement between theory and experiment is excellent, and higher approximations to the theoretical value should even improve the agreement. It is remarkable that the simple first approximation of Kihara gives results which are as good as those given by the very complicated second approximation of Chapman and Cowling.

C. Helium-Hydrogen Mixtures

The properties of gaseous mixtures depend to some extent on the forces between unlike molecules. In principle these forces could be calculated from experimental results on mixtures, but in practice the accuracy required of the experimental measurements is too great, since the dependence of a property on the forces between unlike molecules is partly masked by the dependence on the forces between the like molecules in the mixture. It would, therefore, be very helpful to be able to predict the interaction for unlike molecules from the known interactions for the like molecules. In this way properties of gaseous mixtures could be calculated from data on the pure components. Combining rules for the exp-six potential can be obtained by

Table VII

Comparison of observed values of the thermal diffusion factor for the system D_2-H_2 with those calculated for the exp-six potential.

% H_2	Thermal Diffusion Factor, α_T.			
	$[cc]_1$	$[cc]_2$	$[K]_1$	Obs.
10	.1491	.1552	.1579	.161
20	.1507	.1567	.1590	.160
30	.1525	.1584	.1602	.170
40	.1544	.1602	.1614	.173
50	.1565	.1622	.1628	.173
60	.1588	.1643	.1643	.173
70	.1612	.1666	.1658	.172
80	.1638	.1691	.1675	.176
90	.1665	.1718	.1693	.184

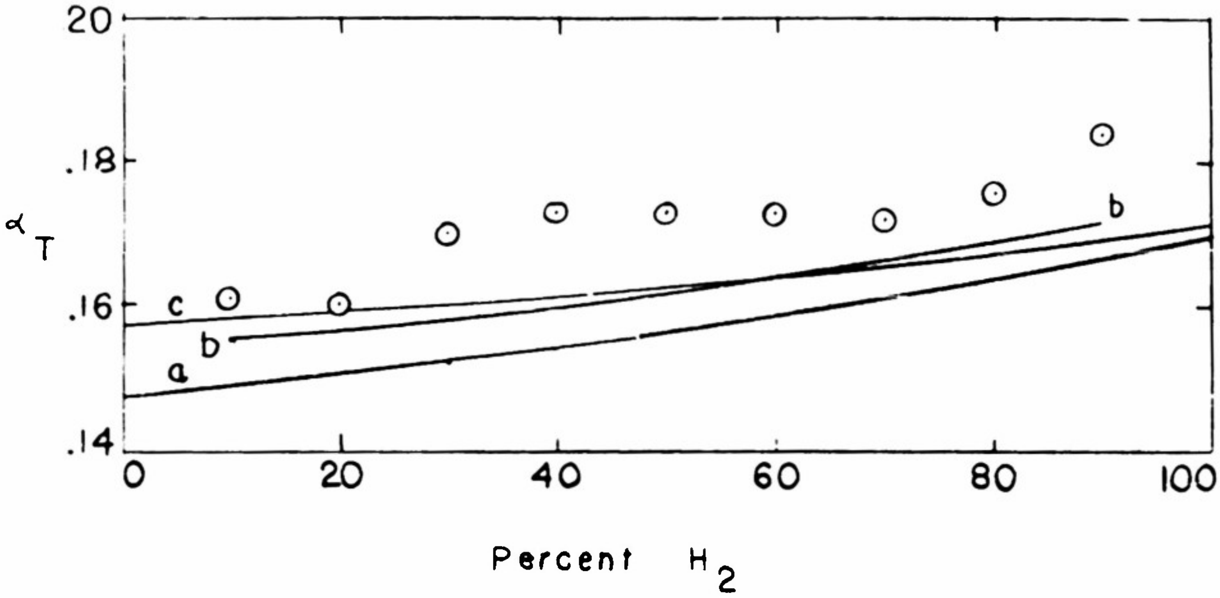

Fig. 8. Comparison of observed values of the thermal diffusion factor α_T for the system D_2-H_2 with those calculated for the exp-six potential. Curves a, b: first and second approximations of Chapman and Cowling; curve c: first approximation of Kihara. Here $\bar{T} = 327^\circ$K.

writing Eq. (1) in the form

$$\varphi(r) = Ae^{-br} - C/r^6 \quad . \tag{20}$$

Zener[42] has shown from theoretical considerations that the parameter b for an unlike interaction may be obtained from the relation

$$b_{12} = \frac{1}{2}(b_{11} + b_{22}) \quad , \tag{21}$$

where b_{12} refers to the unlike interaction, and b_{11} and b_{22} refer to the like interactions. The theory of the dispersion energy leads to the following combining rule[43] for the parameter C :

$$C_{12} = (C_{11} C_{22})^{\frac{1}{2}} \quad . \tag{22}$$

Unfortunately no combining rule for the parameter A is forthcoming from theory, and we must proceed empirically. Since the parameters A and C appear in Eq. (20) in a similar way, it is tempting to write the relation

$$A_{12} = (A_{11} A_{22})^{\frac{1}{2}} \quad . \tag{23}$$

We could also proceed by analogy with Eq. (21) for the parameter b , letting $A = e^a$, and

$$a_{12} = \frac{1}{2}(a_{11} + a_{22}) \tag{24}$$

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(42) C. Zener, Phys. Rev. 37, 556 (1931).

(43) J. A. Beattie and W. H. Stockmayer, States of Matter (D. van Nostrand, New York, 1951, H. S. Taylor and S. Glasstone, Editors), pp. 350-352.

Eqs. (23) and (24) are entirely equivalent, however, as may be shown by substitution of the relation $a = \ln A$ into Eq. (24). We have, therefore, taken this empirical relation as our third combining rule.

The combining rules, Eqs. (21) - (23), are more complicated in terms of the parameters ϵ, r_m, and α. The parameter $(r_m)_{12}$ for the unlike interaction first is found from the transcendental equation.

$$(GH)(r_m)_{12}^7 = \exp\left[H(r_m)_{12}\right], \tag{25}$$

where

$$G = \frac{1}{2}\left[\frac{\alpha_{11}}{(r_m)_{11}} + \frac{\alpha_{22}}{(r_m)_{22}}\right],$$

$$H = (\alpha_{11}\,\alpha_{22})^{-\frac{1}{2}}\left[(r_m)_{11}(r_m)_{22}\right]^{-3}\exp\left[(\alpha_{11}+\alpha_{22})/2\right].$$

The parameters α_{12} and ϵ_{12} are then calculated from the relations

$$\alpha_{12} = G(r_m)_{12}, \tag{26}$$

$$\epsilon_{12} = (\epsilon_{11}\,\epsilon_{22})^{\frac{1}{2}}\left[\frac{(\alpha_{12}-6)^2}{(\alpha_{11}-6)(\alpha_{22}-6)}\right]^{\frac{1}{2}}\exp\left(\frac{\alpha_{11}+\alpha_{22}-2\alpha_{12}}{2}\right) \tag{27}$$

Substitution of the exp-six potential parameters in Table I leads to the following values for the interaction between a helium atom and hydrogen molecule:

$$\begin{aligned} \alpha &= 13.22, \\ r_m &= 3.244\ \text{Å}, \\ \epsilon/k &= 18.27^\circ\text{K}. \end{aligned} \tag{28}$$

A check on the suitability of the combining rules may be obtained by using these parameters to calculate properties of helium-hydrogen mixtures for comparison with available measurements.

The second virial coefficient of a binary mixture, B_m, is given by

$$B_m = x_1^2 B_{11} + x_2^2 B_{22} + 2x_1 x_2 B_{12} , \tag{29}$$

where x_1 and x_2 are the mole fractions of the components, B_{11} and B_{22} are the virial coefficients of the pure components, and B_{12} is the virial coefficient of a hypothetical pure gas whose molecules interact according to the potential law for (1, 2) interactions. Second virial coefficients for helium, hydrogen, and a 50-50 mixture have been measured by Gibby, Tanner, and Masson[24]. Table VIII compares the experimental values of B_{12} as obtained from Eq. (29) with the values calculated from the parameters of Eq. (28). A small quantum correction has been applied to the calculated values, taking the molecular weight to be equal to $\left[2M_1 M_2/(M_1 + M_2)\right]$. The agreement is of the same order as that obtained for the pure components using the parameters of Table I. The viscosity of a binary mixture η_m is given by

$$\eta_m = \frac{1}{X}\left[\frac{1 + Z}{1 + Y/X}\right] , \tag{30}$$

Table VIII

Comparison of observed values of the second virial coefficient interaction term, B_{12}, for He - H_2 mixtures with those calculated from the combining rule for the exp-six potential.

T, °K	B_{12}, cc/mole		
	Calc.	Obs.	Deviation, cc/mole
298.2	14.66	15.60	+0.94
323.2	14.74	15.66	+0.92
348.2	14.71	15.24	+0.53
373.5	14.70	15.61	+0.91
398.4	14.68	14.39	-0.29
423.3	14.64	15.81	+1.17
448.2	14.60	14.55	-0.05

where

$$X = \frac{x_1^2}{\eta_1} + \frac{x_2^2}{\eta_2} + \frac{2x_1x_2}{\eta_{12}} ,$$

$$Y = \frac{3}{5} A_{12}^* \left\{ \frac{x_1^2}{\eta_1} \left(\frac{M_1}{M_2}\right) + \frac{2x_1x_2}{\eta_{12}} \left[\frac{(M_1+M_2)^2}{4M_1M_2}\right] \left(\frac{\eta_{12}^2}{\eta_1\eta_2}\right) + \frac{x_2^2}{\eta_2} \left(\frac{M_2}{M_1}\right)\right\} ,$$

$$Z = \frac{3}{5} A_{12}^* \left\{ x_1^2 \left(\frac{M_1}{M_2}\right) + 2x_1x_2 \left[\frac{(M_1+M_2)^2}{4M_1M_2}\left(\frac{\eta_{12}}{\eta_1} + \frac{\eta_{12}}{\eta_2}\right) - 1\right] + x_2^2 \left(\frac{M_2}{M_1}\right)\right\} ;$$

and η_1 and η_2 are the viscosities of the pure components as given by Eq. (8). The term η_{12} is the viscosity of a hypothetical pure gas whose molecules interact according to the potential law for (1, 2) interactions, and whose molecular weight is $\left[2M_1M_2/(M_1 + M_2)\right]$. The term A_{12}^* is a function of α_{12} and T_{12}^* ($= kT/\epsilon_{12}$) tabulated in reference (1). Figure 9 shows a plot of η_m for He - H_2 mixtures at several temperatures as calculated from Eq. (30). The agreement with the available experimental data[45] seems satisfactory, since it is of the same order as the agreement for the pure components.

A serious test of the combination rules for the exp-six potential is given by the thermal diffusion factor, since this quantity depends strongly on the forces between unlike molecules, and only weakly on interactions between like molecules. The thermal diffusion factor for the system He - H_2 has been

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(45) M. Trautz and K. F. Kipphan, Ann. Physik 2, 743 (1929); M. Trautz and H. E. Binkele, ibid 5, 561 (1930); M. Trautz and I. Husseini, ibid 20, 121 (1934); van Itterbeek, van Paemel, and van Lierde, Physica 13, 88 (1947).

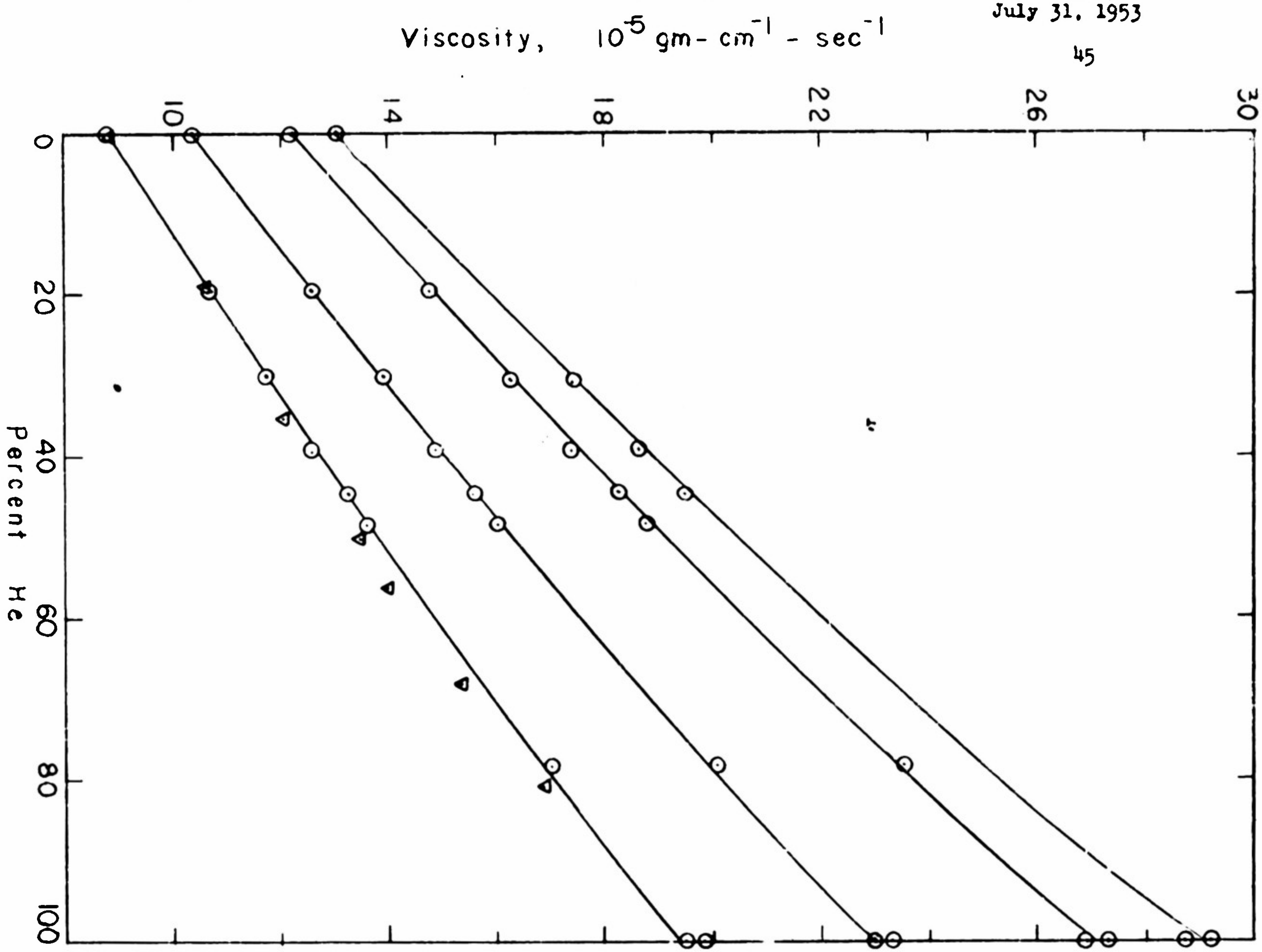

Fig. 9. Comparison of observed and calculated values of the viscosity of helium-hydrogen mixtures. Curves are calculated for the exp-six potential using the combining rules, Eqs. (25)-(27). Observed values: ⊙ Trautz, et al; ▽ van Itterbeek, van Paemel, and van Lierde (291.7°K).

measured by the thermal separation method by a number of workers[46], whose results are in reasonable accord with one another. The scatter of the experimental results is greater than the difference between Kihara's first approximation and Chapman and Cowling's second approximation, and we have, therefore, used Kihara's expression since the second approximation of Chapman and Cowling requires very tedious calculations. Figure 10 shows a comparison between calculated and experimental values of the thermal diffusion factor, α_T, as a function of composition for three different values of the mean temperature, $\bar{T}$, as given by Eq. (18). We have not extended the comparison to mean temperatures in which one bulb of the separation system was at a temperature below 90°K because of the uncertainty of the quantum corrections at low temperatures. The agreement is within the experimental error in all cases. Within the experimental error the calculated value of α_T is independent of temperature over this range, in agreement with the observations of Grew[46].

Thermal diffusion in the system D_2 - He is of particular interest since the observed separation cannot depend on the difference in mass, but most arise from the law of force. Figure 11 is a comparison of the measured[40]

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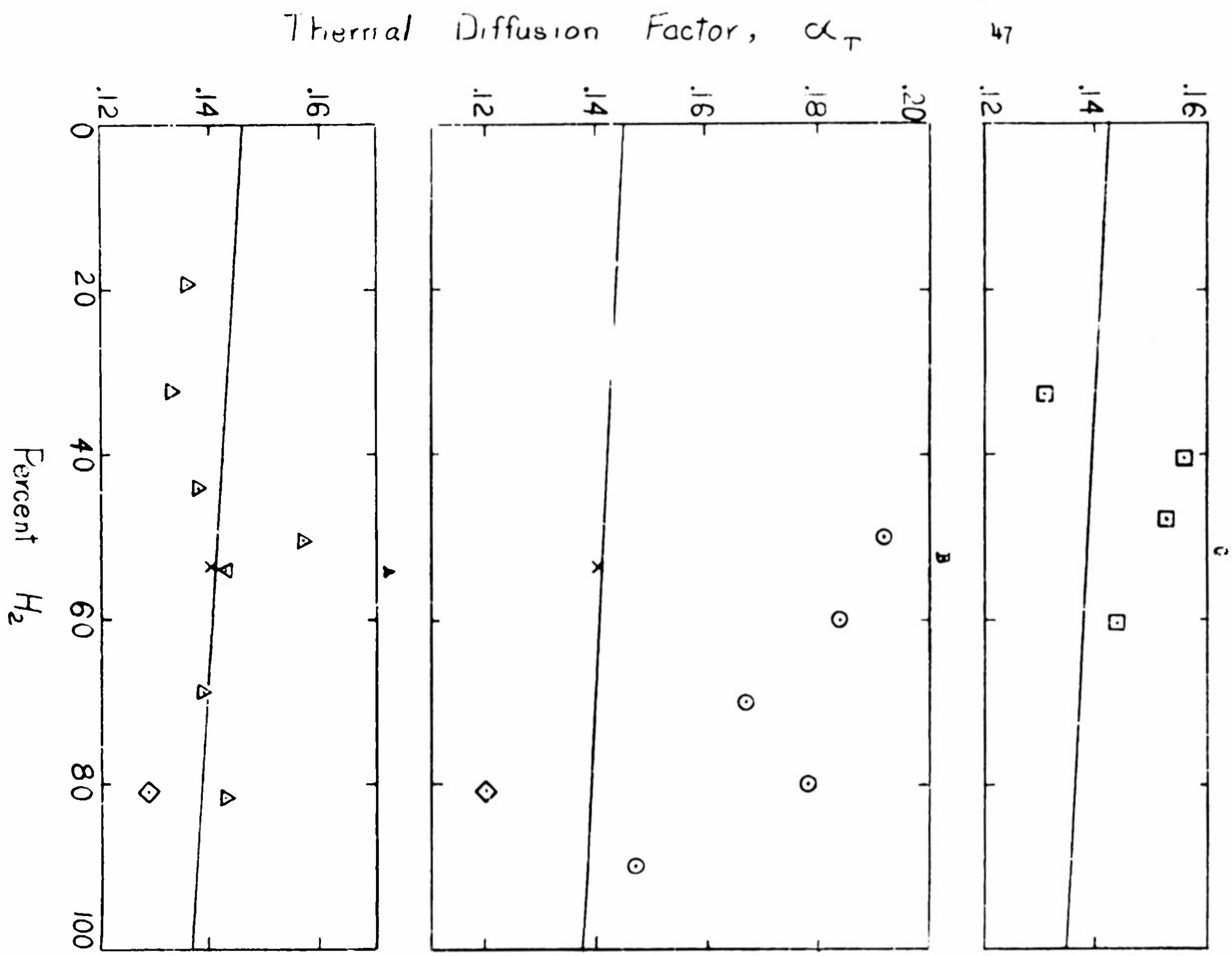

Fig. 10. Comparison of observed values of the thermal diffusion factor α_T for the system He – H_2 with those calculated for the exp-six potential according to Kihara's approximation. A. $\bar{T}$ = 436°K. B. $\bar{T}$ = 327°K. C. $\bar{T}$ = 153°K. Observed values: ⊡ Elliet and Masson; ⊙ Heath, Ibbs, and Wild; △ van Itterbeek, van Paemel, and van Lierde; ◇ Murphey; × Grew; ▽ de Troyer, van Itterbeek, and Rietveld.

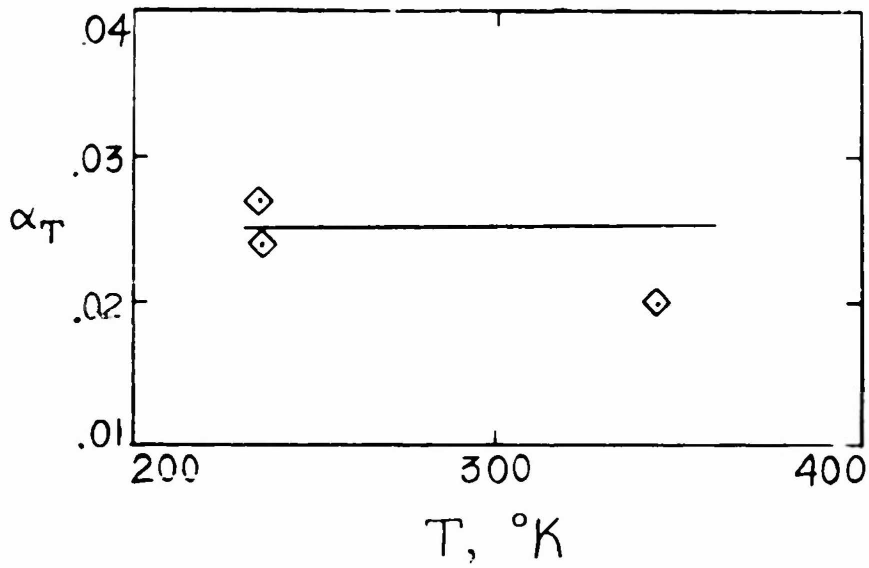

Fig. 11. Comparison of observed and calculated values of the thermal diffusion factor α_T as a function of temperature for the system D_2 - He at a composition of 20 percent D_2.

and calculated values of α_T for $D_2 \cdot He$ as a function of temperature at a composition of 20 percent deuterium. The agreement is probably satisfactory, in view of the rather large experimental errors involved in measuring thermal separations for this system.

In summary, the agreement between theory and experiment for second virial coefficients, viscosities, and thermal diffusion factors for mixtures of helium and hydrogen greatly increases our confidence in the accuracy of the combining rules, Eqs. (25)-(27), for the exp-six potential.

APPENDIX

Table of Force Constants for Some Simple Non Polar Molecules.

Parameters for the Modified Buckingham (6-exp) Potential						
Substance	Parameters			Experimental Data Used for Determination of the Parameters		
	r_m (Å)	ϵ/k (°K)	α	Viscosity Coefficients	Second Virial Coefficients	Crystal Properties
H_2	3.337	37.3	14.0	d	e	-
He	3.135	9.16	12.4	f	g	-
Ne	3.147	38.0	14.5	h	i	j
A	3.866	123.2	14.0	k	l	j
Kr	4.056	158.3	12.3	-	m	j
Xe	4.450	231.2	13.0	-	n	j
CH_4	4.206	152.8	14.0	o	p	q
N_2	4.040	113.5	16.2	-	r	q
	4.011	101.2	17.0	s	-	-
CO	<4.099	>132.0	>17	-	t	q
	3.937	119.1	17.0	u	-	-

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